(12) UK Patent Application (19) GB (11) 2 331 622 (13) A

(43) Date of A Publication 26.05.1999

(21) Application No 9825566.4

(22) Date of Filing 20.11.1998

(30) Priority Data
(31) 19751401 (32) 20.11.1997 (33) DE

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(51) INT CL^6
H01J 49/42

(52) UK CL (Edition Q)
H1D DMD D21B D44 D51

(56) Documents Cited
EP 0270232 A WO 98/05039 A US 5170054 A
US 2939952 A

(58) Field of Search
UK CL (Edition P) H1D DMD DMF DMG DMH
INT CL^6 H01J 49/42

(54) Abstract Title
Quadrupole RF ion traps

(57) The invention relates to quadrupole RF ion traps for use in a mass spectrometer, either as storage elements or as mass separators for the measurement of the mass spectrum of stored ions. The invention particularly relates to ion traps, which should show a pure quadrupole field without superimpositions of higher multipoles or a quadrupole field with superimposition of one or several higher multipole fields of a precisely defined intensity, but no others, particularly no higher multipole fields.

The limitation of ring and end cap electrodes to finite dimensions induces components of higher multipole fields within the ion trap, which may cause negative influences on the storage and scanning behaviour. The invention consists of strongly suppressing the formation of higher multipole fields other than those required, by reduction of the gap width between the electrodes in the marginal area, compared to the gap width of electrodes modelled exactly according to the equipotential surfaces of the required field mixture of infinite expansion. A particularly strong suppression of higher multipole fields can be achieved by a wave-shaped constriction in the marginal area between the electrodes. Fig 3 shows the field lines between the ring electrode (1) and an end cap electrode (2).

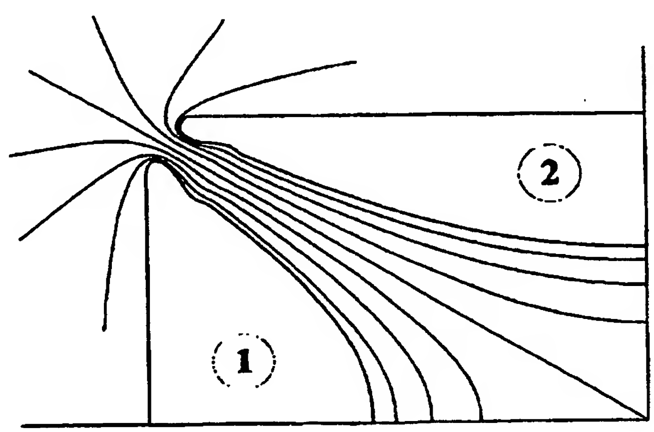

Figure 3

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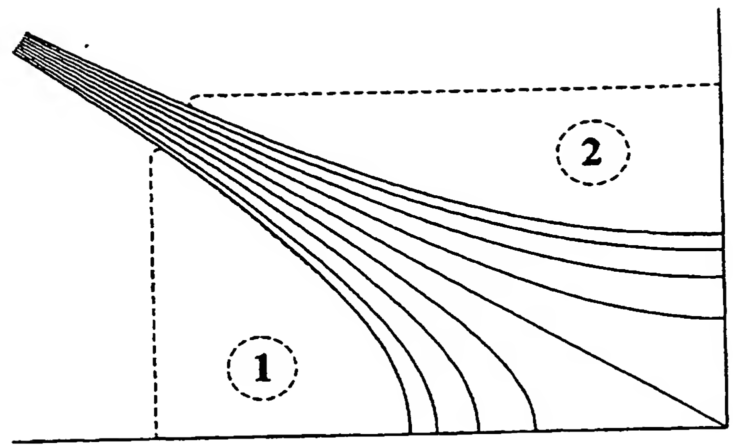

Figure 1

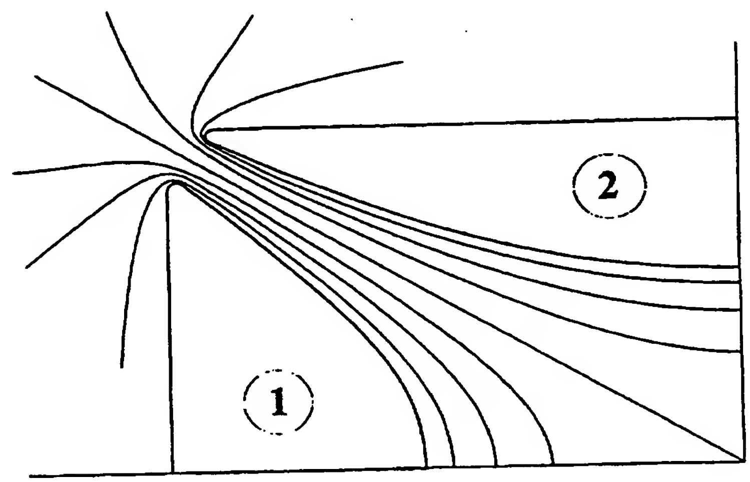

Figure 2

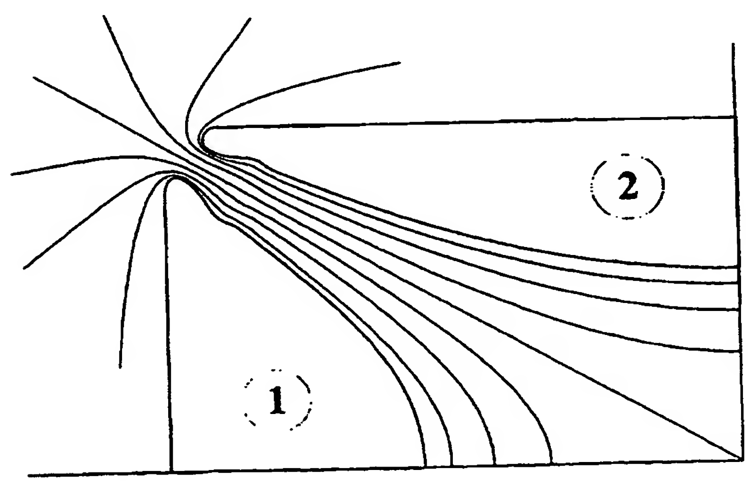

Figure 3

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Quadrupole RF Ion Traps

The invention relates to quadrupole RF ion traps of the kind used in mass spectrometers, either as storage elements or as mass separators for the measurement of the mass spectrum of stored ions.

Theory and various applications of RF quadrupole ion traps as tandem mass spectrometers for MS/MS analyses, as reaction containers and measurement instruments for ion-molecule reactions, as tools for selective storage of ions with a uniform mass-to-charge ratio, or for the fragmentation of ions for analyses of their structure, are known from the standard book: "Practical Aspects of Ion Trap Mass Spectrometry", Volumes I, II, and III edited by R. E. March and John F. J. Todd, CRC Press, Boca Raton, New York, London, Tokyo, 1995.

The electrode form for the generation of an "ideal" quadrupole field was first described by Wolfgang Paul and Helmut Steinwedel in DE 944 900 and US 2,939,952, namely one in which the ring and end cap electrodes each have a rotationally symmetrical surface form with a hyperbolic cross section, the hyperbolas for the ring and end caps belong to a hyperbola family with identical asymptotes, and the asymptotes have an angle of $\mathrm{tang}(\alpha) = \sqrt{2}$ to the axial direction.

A pure quadrupole field without superimposition of higher multipole fields is however generated by this arrangement only if the electrodes extend infinitely, which cannot be realised for practical reasons. Any truncation of the electrode form to finite dimensions, necessary for a finite size of the instrument, but also for reasons of finite electrical capacity of the electrode structure, involves a distortion of the quadrupole field which corresponds mathematically to the superimposition of weak multipole fields with a higher order.

The superimposition of the RF quadrupole field with higher multipole fields has severe, sometimes even dramatically severe effects on the stored ions, even if the multipole fields are relatively weak. The effect of the higher multipole fields only becomes apparent outside the centre of the trap, i.e., if the ions are not located in the centre of the quadrupole field. The oscillations of the stored ions are normally decelerated by a damping gas so that they collect in the centre of the ion trap. However, the amplitude of their secular oscillations can sometimes temporarily extend into the non-central areas of the ion trap. This can happen (a) when the ions are introduced from the outside into the ion trap or are generated outside the centre inside the ion trap; (b) when the ions are excited by additional electrical fields in their secular oscillation (for example during collisionally induced fragmentation of the ions); and (c) when the ions are ejected from the ion trap mass-selectively for analysis.

An experimental analysis (Alheit et al., "Higher order non-linear resonances in a Paul trap", Int. J. Mass Spectrom. and Ion Proc. 154, (1996), 155-169) demonstrates impressively how specific ions from an actually ideal, though spatially limited ion trap are ejected almost immediately if they are not collected in the center by a damping gas, due to numerous non-linear resonances, generated by extremely weak higher multipole fields, occurring in regular patterns of the Mathieu stability diagram. Non-linear resonances result when the overtones of the ion oscillations, which arise due to non-linear (inharmonic) retroactive forces, encounter the frequencies of the so-called Mathieu side bands. In this way it is possible for the affected ions to acquire energy from the storage field and thus quickly increase their oscillation amplitude (see the above cited standard work, Chapter 3, regarding non-linear ion traps).

The effect of higher multipole fields, relative to the suitability of the ion trap as a mass spectrometer, can be advantageous, but also extremely disadvantageous. The higher

multipole fields have the strongest influence on the various types of mass-selective ion ejection. They can dramatically improve or diminish the mass resolving power of the scan (using a so-called scan method) at the same scan speed. They can even delay or accelerate the ejection of individual ion types with specific dielectric characteristics, as compared to other ions of equal mass-to-charge ratios. The mechanism for these so-called mass shifts (see Chapter 4 of the above cited standard work) is not yet understood. However, a false mass-to-charge-ratio is simulated in this way, and the mass spectrometer loses its intended function as a measuring instrument for the mass-to-charge ratio of the ions.

The generation of quadrupole fields with the superimposition of specific multipole fields of even ordinal numbers, which are especially favourable for the method of "mass-selective instability scans" according to EP 0 113 207, is known from EP 0 321 819 and is based upon a particular shape of electrode. Random superimposition with weak hexapole and octopole fields is possible without higher multipole fields, such as are required for the "non-linear resonance ejection" scan method according to EP 0 383 961. This is described in DE 40 17 264 and is also based upon a particular shape of the electrodes.

The electrode surfaces for a pure quadrupole field according to DE 944 900 and those for superimposition with pure octopole and hexapole fields according to DE 40 17 264 are both shaped as finite sections of computed equipotential surfaces of the required fields. The basis for the computation is that the equipotential surfaces extend infinitely. However, as already mentioned above, truncation of the electrodes to a practical size already involves an undesirable superimposition with higher multipole fields, which has in many cases a detrimental effect upon the scan method being used.

At the same time, multipole fields of measurable strength up to very high orders appear with alternating signs, i.e. the

higher fields are partially added to, partially subtracted from the quadrupole field. In this way, the retroactive pseudoforces, responsible for the secular oscillations of the ions, no longer increase simply linearly with the distance from the centre, but rather have a very complicated characteristic. As a consequence of this, a complicated dependency results, which is no longer manageable, of the secular oscillation frequency on the oscillation amplitude. It is this which finally determines the resolution of the ion-ejecting scan method.

Using simple mathematical simulation methods in computers, it is possible to optimise the octopole and hexapole fields for various scan methods. These simulations, however, no longer agree with experimental results if higher multipole fields arise to a weak, but significant extent, due to limitation of the electrodes. Exact simulation with fields using truncated electrodes is very difficult.

Not only are the mathematical simulations impaired, but also many partially undesirable effects appear in the ion traps. These also affect - in addition to the above mentioned disadvantages - the ability to store ions uniformly during ionization, or the storing of daughter ions during fragmentation.

In general, any type of combination of quadrupole and higher multipole fields can be generated in an ion trap by computing the ideal equipotential surfaces of the field mixture and exactly reproducing the shape of these equipotential surfaces by metallically conducting electrodes. However, it is also necessary for the electrodes to extend for quite a distance toward infinity, to avoid the otherwise inevitable marginal disturbances.

The real equipotential surfaces within a truncated ion trap diverge considerably from the ideal ones before reaching the electrode margins. They concentrate near to the surface of the

electrode edges (see Figure 2) and thin out in the centre between the electrodes. In the space beyond the margins, they diverge strongly from one another and fill the geometrically available space outside the metallically conductive structures. The distribution of equipotential lines in the gap at the margin of the electrodes is thus considerably different from the distribution that they would have with unlimited continuation of the electrode form (Figure 1). The result is a superimposition of the ion trap field with weak higher multipole fields. The exact form of the divergence furthermore depends on the geometric potential distribution outside the ion trap, which again refers back to the geometric construction of the mechanical holder and the environment of the electrodes.

It is therefore desirable to provide a form of electrodes for a quadrupole RF ion trap of finite size, which provides a desired field, for example a pure quadrupole field or a quadrupole field with specific higher multipole fields of a defined intensity superimposed, with the least possible superimposition of other multipole fields of higher order.

According to the invention, there is provided, an RF ion trap having a rotationally symmetrical ring electrode, two rotationally symmetrical end cap electrodes, and means for applying RF voltages to the said electrodes so as to generate a pure quadrupole field, or a quadrupole field having one or more higher multipole fields of a desired type and intensity, wherein the electrode surfaces within the ion trap have a shape corresponding to portions of ideal equipotential surfaces of infinite extent for the generation of the said quadrupole field, and wherein the gap width between the ring and cap electrodes is, in the region of the margin of the ring and cap electrodes, smaller than the gap width which would correspond to the ideal profile of the equipotential surfaces.

In another aspect, the invention provides an RF ion trap for a mass spectrometer with a rotationally symmetrical ring electrode and two rotationally symmetrical end cap electrodes,

wherein the electrode surfaces within the ion trap are modelled on the infinitely expanded, ideal equipotential surfaces for the generation of a quadrupole field, if necessary with superimposition of required higher multipole fields of a defined type and intensity, and the gap width between the ring and end cap electrodes is formed smaller toward the margin than that which corresponds to the ideal profile of the equipotential surfaces.

It is the basic idea of the invention to reduce the influence from the limitation of the electrodes by slightly constricting the bundle of equipotential surfaces at the margin of the electrodes by narrowing the gap width between the electrodes, principally to avoid a premature divergence. Within the gap the constricted bundle of equipotential surfaces widens toward the centre of the ion trap somewhat divergently again, and thus assumes approximately the form and distribution that it would have with infinitely extended electrodes.

The correction is not precise, though it can suppress the formation of undesirable higher multipole fields within the ion trap by more than one order of magnitude. A slight hypercorrection here can particularly minimise the formation and influence of negatively superimposed multipole fields of the even orders 6 - 10 (dodecapole to icosipole). Higher multipoles with odd orders of magnitude do not occur as long as the ion trap is designed symmetrical to the ring mid level, though production tolerances play an extremely important role here. An especially good correction can be achieved by a wave-shaped constriction tapering toward the inside of the ion trap.

Description of the figures

Figure 1 shows a cross-section through the ideal equipotential surfaces of a quarter of an ion trap. These "ideal" equipotential surfaces are computed for a trap of infinite size. Virtually truncated ring (1) and end cap electrodes (2) are shown with a broken line.

Figure 2 shows a cross-section though a quarter of an ion trap with truncated ring and end cap electrodes (the external supporting structure is not shown for clarity). The shapes of the electrodes are modelled as a section of the ideal equipotential surfaces. As can be seen, the "real" equipotential surfaces visibly diverge in the gap area, compared to their "ideal" counterparts according to Figure 1. Outside the ion trap, they uniformly fill the entire available space. For simplicity, no other metal surfaces are shown outside the idealised ion trap, such as would be present in a real ion trap.

Figure 3 shows how "ideal" equipotential surfaces inside the trap can be approximated by a protruding constrictions with a wave-like taper inside the ion trap again towards an ideally shaped electrode form in the trap centre. Using this configuration, superimposition of the field within the ion trap with higher multipole fields remains minimal. Due to the deformation of the margin, the influence of the external holding structure on the inner field is also greatly reduced.

The invention seeks to minimise the formation of any fields other than the required mixture of multipole fields within the ion trap. Superimposition of a quadrupole field with hexapole and octopole fields, sometimes of even higher multipole fields, may certainly also be desirable, as is already apparent from the patents cited initially.

The hexapole field has a non-linear resonance of extreme intensity for the oscillations of ions in an axial direction of the ion trap at exactly one third the frequency of the applied RF voltage. This non-linear resonance can be used very efficiently for a very fast, mass-precise ejection of ions. The increase with time of the oscillation amplitude of the ions in an axial direction follows a hyperbolic function in the vicinity of a mathematical pole of the function. That leads to rapid ejection of ions and thus to an excellent mass resolving power, even with very fast scan methods. Fast scan methods means more spectra from more samples per unit of time, forming an important factor in the profitability of the mass spectrometer. Fast scan methods are

however also important in keeping pace with a constantly improved separation power of upstream chromatographic or electrophoretic separation methods for substance mixtures.

On the other hand, the octopole field has a damping effect on any type of resonant ejection, because it generates a relatively strong shift of the oscillation frequency of an ion with an increase in its oscillation amplitude. Thus the ion falls out of resonance as soon as its oscillation amplitude rises. This damping of resonance works for all resonant disturbances, for example for ripple disturbances on the quadrupole RF, for dipolar excitations through excitation frequencies across the end cap electrodes and for all types of non-linear resonances. An octopole field, not too weak, even chokes off the effect of its own non-linear resonance in an axial direction of the ion trap at a quarter of the quadrupole RF. In this way, the octopole field is extraordinarily beneficial for the good and safe storage of ions.

The hexapole field also generates a shift in the oscillation frequency with increasing amplitude, but only of the second order. This shift is directed against the octopole field shift and counterbalances this, although only weakly. With a combination of a relatively strong hexapole field with a weaker octopole field, an excellent scan method according to the method of non-linear ion ejection thus results. Since however the effect of all non-linear resonances disappears at the centre of the ion trap, the ions have to be push-started by dipolar excitation of the ion oscillations using an alternating current between the end caps, as described in DE 689 13 290.

The generation of a relatively strong hexapole field is already possible using extraordinarily minimal form changes of the electrodes. The electrode forms for the superimposition with pure octopole and hexapole fields are described in DE 40 17 264, whereby this patent describes the electrode surfaces by such equipotential surfaces, which are provided by an infinite

expansion of the field. With a truncation of the electrodes to a practically producible and usable form, the above described problems with the generation of other higher multipole fields thus occur.

The ions do not need absolutely to be ejected by a non-linear resonance of the hexapole field. Through non-linear resonances of higher uneven multipole fields, higher mass ranges can be used at the same maximum RF voltage. As described in DE 43 16 738, a superimposition of the quadrupolar RF field with another quadrupolar alternating field of a lower frequency can also be used advantageously to eject the ions. This quadrupolar alternating field can be generated solely using electrical media; no form change to the electrodes is necessary for this. Here the hexapole field can be completely ignored, although an octopole field is also favourable in this place, although unnecessary.

The question arises, how can the generation of higher multipole fields be avoided, in view of the limitation of the electrode sizes.

As outlined above, the multipole fields are generated by marginal disturbances of the field. The bundle of equipotential surfaces already diverges within the gap range between the electrodes, as seen in Figure 2, in contrast to the bundle of ideal equipotential surfaces of an infinitely extended arrangement according to Figure 1.

Normally, the electrodes at the edges of the limitation are not angularly shaped, but instead are rounded off. This rounding off of electrode edges is necessary to prevent electrical discharges in the intensified field from angular edges (peak discharges). The risk of discharges is increased even further by the presence of damping gases with pressures between 10-2 to 10-4 hectopascal. However, these rounded edges intensify the marginal effect on the equipotential surfaces.

The divergence of the equipotential surfaces can be at least partially counteracted by a constriction of the gap area in a relatively simple manner.

Quite favourable for preventing higher multipole fields is a simple constriction of the gap by two respectively opposing, rounded protrusions at the edge of the electrodes in the direct marginal area. The bundle of equipotential surfaces is compressed here between the protrusions in the area of the outlet from the ion trap. Here, the compression is stronger directly at the surface of the protrusions than at the centre between the protrusions. The bundle of equipotential surfaces then widens again toward the centre of the ion trap again, whereby especially the bundle parts severely narrowed in the direct surface area of the projections are relieved. In this way, the equipotential surfaces are distributed within the ion trap more similar to an ideal, infinitely extended arrangement than with a simple, protrusionless truncation of the electrodes.

Optimal conditions are created with constrictions through two respective rounded, opposing projections, the thickness of which together equals about 15% of the gap width. Optimal constriction is however dependent on many parameters and can vary within a range of about 5% to 40%. The projections can, for example, have a hemispherical profile, although a somewhat flatter design is more favourable. The optimal shape of the projections is especially dependent on the shape of the equipotential surfaces in the area outside the ion trap.

It may be favourable to have projections of asymmetrical thickness. It is an especially disturbing effect if the remaining higher multipole fields of the orders 4 - 10 (or even higher) have negative signs, such as occur with un-constricted gaps. With thicker protrusions on the ring electrode and thinner ones on the

end caps, this tendency can be counteracted in such a way that the remainder of the higher multipoles receive positive signs.

Even better than simple projections is, however, an electrode edge in the form of a wave tapering toward the inside of the ion trap. Here, the outer protrusion first transforms into a slight depression, which only then becomes rounded off into the ideal form of infinitely expansive equipotential surfaces, as shown in Figure 3. The wavelength here should be in the order of magnitude of the gap width. This wave shape in the marginal area can (particularly with narrow gap widths) also be continued over several continuously weakening wave cycles toward the inside; this corresponds precisely to the reciprocal process of an apodization of the light beam at the margins of an optical gap for preventing the wave-shaped margins of the diffraction images. At the inside end of the waveband there is then a distribution of equipotential surfaces beyond the gap, which corresponds in density and direction to a very good approximation of an infinitely expanded field distribution. In this way, the effect of the marginal disturbance within the ion trap is practically disabled.

The wave can be simulated in a simpler embodiment through a medium profile of constriction. This results in a continuous constriction toward the margin. A particularly simple embodiment of this type of constriction is when the hyperbolic profile of the electrode surfaces toward the gap margin very simply turns into an straight form. This form can be reproduced in manufacturing with very good production tolerances and also easily tested, whereas the reproducible manufacturing of a wave-shaped gap termination requires highly skilled workmanship and high mechanical precision.

The manufacturing tolerances for the inner surface of an ion trap must be a maximum of about 3 micrometers for a trap with a ring diameter of about 2 centimetres, if ion traps with reproducible operation must be achieved.

Optimization of the electrode forms is not simple, since the optimal form is dependent upon the external design of the ion trap, even from the dielectrics present outside the trap. Using the above given basic principles however, the experienced specialist will succeed in extensively suppressing the occurrence of higher multipoles, even without special calculations, but by feel, so to speak.

In the outer space, each of the end cap electrodes usually becomes flange-shaped, which forces the equipotential surfaces more strongly toward the ring electrode. This tendency may be countered by an asymmetrically shaped wave. On the ring electrode, a protrusion of about +9% of the gap width, a wave trough of -3% of the gap width, and a terminating protrusion of +1% of the gap width may be formed. On the end cap, the corresponding dimensions then should be +6%, -2% and +0.6%. For more precise work, it may be necessary to calculate the potential distribution very precisely within the ion trap using an optimization program and compare this with the ideal distribution. For this comparison, it is sufficient to compare the ideal and real potential characteristic within the rotation axis (usually called the z axis), since this potential characteristic alone describes and defines all potential distributions in the vicinity. Such a program for potential calculation may be based, for example, on the method of finite elements.

Experimental optimization of forms is difficult, particularly since there are no simple measurement parameters to ensure success.

CLAIMS

1. An RF ion trap having a rotationally symmetrical ring electrode, two rotationally symmetrical end cap electrodes, and means for applying RF voltages to the said electrodes so as to generate a pure quadrupole field, or a quadrupole field having one or more higher multipole fields of a desired type and intensity,
wherein the electrode surfaces within the ion trap have a shape corresponding to portions of ideal equipotential surfaces of infinite extent for the generation of the said quadrupole field, and wherein the gap width between the ring and cap electrodes is, in the region of the margin of the ring and cap electrodes, smaller than the gap width which would correspond to the ideal profile of the equipotential surfaces.

2. An RF ion trap as claimed in Claim 1, wherein the means for applying RF voltage includes means for superimposing a hexapole and/or an octopole field on the quadrupole field.

3. An RF ion trap as claimed in any one of the preceding claims, wherein the constriction of the spacing between the ring and end cap electrodes corresponds to about 5% to 40% of the theoretical gap width.

4. An RF ion trap as claimed in Claim 3, wherein the constriction of the spacing between the ring and end cap electrodes corresponds to about 15% of the theoretical gap width.

5. An RF ion trap as claimed in any one of the preceding claims, wherein the spacing between the ring and end cap electrodes is constricted asymmetrically.

6. An RF ion trap as claimed in any one of the preceding claims, whereby the cross sections of the ring and/or end cap electrodes, which are hyperbola-like within the ion trap, are straight in the region of the margin of the electrodes.

7. An RF ion trap as claimed in any one of Claims 1 to 5, wherein the constriction of the gap width has the form of

two respective opposing, rounded-off protrusions at the margins of the electrodes in the gap region.

8. An RF ion trap as claimed in Claim 7, wherein the depressions are formed inside the ion trap adjacent to the marginal portions of the gap, whereby a wave is formed in the electrode surfaces in the marginal area.

9. An RF ion trap as claimed in Claim 8, wherein the wave includes a plurality of cycles, the amplitude of which decreases with distance from the margin of the electrodes.

10. A method of operating an RF ion trap, which method comprises providing an ion trap having a rotational symmetrical ring electrode and two rotationally symmetrical end cap electrodes, and applying an RF voltage to the said electrodes so as to generate a pure quadrupole field, or a quadrupole field having one or more higher multipole fields of a desired type and intensity,
wherein the electrode surfaces within the ion trap have a shape corresponding to portions of ideal equipotential surfaces of infinite extent for the generation of the said quadrupole field, and wherein the gap width between the ring and cap electrodes is, in the region of the margin of the ring and cap electrodes, smaller than the gap width which would correspond to the ideal profile of the equipotential surfaces.

11. A method of operating an RF ion trap substantially as hereinbefore described with reference to and as illustrated by the accompanying drawings.

12. An RF inon trap substantially as hereinbefore described with reference to and as illustrated by the accompanying drawings.

13. An RF ion trap for a mass spectrometer with a rotationally symmetrical ring electrode and two rotationally symmetrical end cap electrodes,
wherein the electrode surfaces within the ion trap are modelled on the infinitely expanded, ideal equipotential surfaces for the generation of a quadrupole field, if

necessary with superimposition of required higher multipole fields of a defined type and intensity, and the gap width between the ring and end cap electrodes is formed smaller toward the margin than that which corresponds to the ideal profile of the equipotential surfaces.

14. An RF ion trap as claimed in Claim 13, wherein a hexapole and/or an octopole field is superimposed on the quadrupole field as required higher multipole fields.

15. An RF ion trap as claimed in Claim 13 or Claim 14, wherein the constriction of the spacing between the ring and end cap electrodes corresponds to about 5% to 40% of the spacing.

16. An RF ion trap as claimed in any one of Claims 13 to 15, wherein the constriction of the spacing between the ring and end cap electrodes corresponds to about 15% of the spacing.

17. An RF ion trap as claimed in any one of Claims 13 to 16, wherein the spacing between the ring and end cap electrodes is constricted asymmetrically.

18. An RF ion trap as claimed in any one of Claims 13 to 17, whereby the hyperbola-like forms of the ring and/or end cap cross-sections each become straight in the gaps towards the margin of the electrodes.

19. An RF ion trap as claimed in any one of Claims 13 to 17, wherein the constriction of the gap width has the form of two respective opposing, rounded-off protrusions at the margins of the electrodes in the gap area.

20. An RF ion trap as claimed in Claim 19, wherein the protrusions toward the inside of the ion trap change into slight, rounded-off depressions contrasted to the ideal profile of the surfaces, so that the electrode surfaces in the marginal area assume the form of a slight wave.

21 An RF ion trap as claimed in Claim 20, wherein the projections toward the inside of the ion trap change into a weakened wave form with several cycles.

22. A mass spectrometer including an ion trap as claimed in any one of Claims 1 to 9, or Claims 12 to 21.

The Patent Office

Application No: GB 9825566.4
Claims searched: all

Examiner: Russell Maurice
Date of search: 15 December 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): H1D (DMD, DMF, DMG, DMH)

Int Cl (Ed.6): H01J (49/42)

Other: Online WPIL

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X,Y	EP 0270232 A	Griffiths (see abstract)	X: 1, 5, 10, 13 & 17 Y: 2 & 14
X, P	WO 98/05039 A	VARIAN (see figure 5)	X: 1, 6, 10, 13 & 18
Y	US 5170054 A	Franzen (see whole document)	Y: 2 & 14
A	US 2939952 A	Paul et al (see whole document)	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.